REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
12-17-2008	FINAL REPORT	09-15-2006 TO 09-14-2008

4. TITLE AND SUBTITLE
CARBON FIBER NANOTUBE REINFORCED ALUMINA NANOCOMPOSITE

5a. CONTRACT NUMBER
FA9550-06-C-0138

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
EDWARD J. YADLOWSKY, C. CHRISTOPHER KLEPPER,
W.G. FAHRENHOLTZ, G.E. HILMAS

5d. PROJECT NUMBER
067

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
HY-TECH RESEARCH CORPORATION
104 CENTRE COURT
RADFORD, VIRGINIA 24141

8. PERFORMING ORGANIZATION REPORT NUMBER
067-FR

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
USAF, AFRL
AF OFFICE OF SCIENTIFIC RESEARCH
875 N. RANDOLPH ST., ROOM 3112
ARLINGTON, VA 22203
ROLAND P. HOWARD 703-696-5926

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2013-0966

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution Statement A. Approved for public release. Distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Demonstrated in situ nucleation of Fe and Co catalytic nanoparticles in alumina powders by heating metal salts in reducing atmospheres or in polyethylene glycol. Carbon nanotubes(CNT) were synthesized in situ by heating the resulting mixtures in acetylene, xylene, or ethanol vapors. An acid purification process was developed by the STTR partner, Missouri Science and Technology University (MST), to disperse commercially produced CNTs, which are initially hydrophobic, in an aqueous alumina slurry. MST demonstrated the first pressureless sintering of alumina- CNT nanocomposites. The 25% fracture toughness enhancement observed with addition of 1% commercial CNTs decreased at higher concentration levels due CNT entanglement.

Efficient induction heating of highly conductive ZrB2-LaB6 eutectic samples was demonstrated in a single mode microwave resonator by positioning the load where it presents minimum impedance to the resonator, i.e. where the electric field is a minimum. Powder loads allows penetration of microwave field to provide volume heating if powder size is smaller than skin depth. Results indicate feasibility of employing the ver

15. SUBJECT TERMS
CARBON NANOTUBES

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			EDWARD J. YADLOWSKY
					19b. TELEPHONE NUMBER *(Include area code)* 540-639-4019

April 2008 Report
Missouri S&T Sub-contract in support of
"In-Situ Synthesis of Carbon Nanotubes for Reinforcement of Alumina"

FA9550-06-C-0138

Report submitted to:
Dr. Ed Yadlowsky
Hy Tech Research Corporation

Report Prepared by:
Shi Zhang, Bill Fahrenholtz, and Greg Hilmas
University of Missouri-Rolla

April 8, 2008

Overview

This report summarizes recent work at the Missouri University of Science and Technology (Missouri S&T). The main focus of the work has been characterization and testing of alumina-CNT composite materials. To our knowledge, this is the first process developed for densification of Al_2O_3-CNT materials that does not involve pressure-assisted methods such as hot pressing or spark plasma sintering. In addition, a series of SiC pellets was prepared and shipped to Hy-Tech for microwave sintering studies. Finally, pellets of a LaB_6-ZrB_2 eutectic are being prepared for additional studies at Hy-Tech and microwave dielectric measurements at Oak Ridge National Laboratory.

Alumina-CNT composites

During this quarter, progress was made on the densification of Al_2O_3-CNT composites. In the report dated January 10, 2008, it was noted that the CNTs were depleted near the outer edges of pellets during sintering. Initially, an attempt was made to enrich the sintering atmosphere using a CO-CO_2 mixture, but that led to more pronounced oxidation of the nanotubes. Subsequently, the Al_2O_2-CNT pellets were packed in graphite powder for densification. The resulting pellets retained all of the CNTs with no depletion near the edges. Using the new method, mixtures of commercial alumina powder (Malakoff RC-HP) and commercial CNTs were densified to ~98% relative density by pressureless sintering at 1600°C.

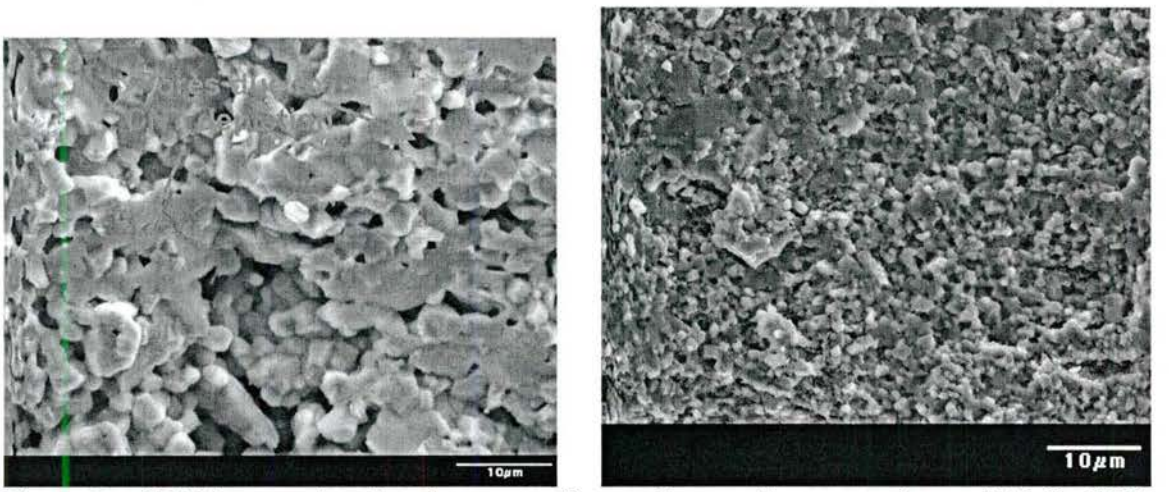

Figure 1. SEM images showing the near surface regions on fracture surfaces of Al_2O_3-CNT pellets. The image on the left is a pellet sintered in flowing argon that shows depletion of the CNTs from a region about 200 μm deep from the surface. The image on the right is from a pellet sintered packed in graphite powder that had no depletion of the CNTs.

The microstructures of three Al_2O_3-based composites were examined. The ceramics were prepared from three different powders: 1) P-55 supplied by Hy-Tech, which was treated in the carbonizing gas, but that did not contain Fe seed particles; 2) P-56 supplied by Hy-Tech, which was treated in a carbonizing gas; and 3) a mixture of alumina and commercial CNTs prepared at Missouri S&T.

Figure 2 shows the microstructure of the composite prepared from Hy-Tech powder P-55, which underwent treatment in the carbonizing gas, but did not have Fe nanoparticles incorporated into it. The powders were sintered to 98% relative density at 1600°C. Mass change measured by thermal gravimetric analysis (TGA) indicated that the material contained about 1.5 vol.% carbon. In this material, the carbon appeared to be uniformly distributed through the matrix. The carbon may or may not have crystallized to graphite during sintering.

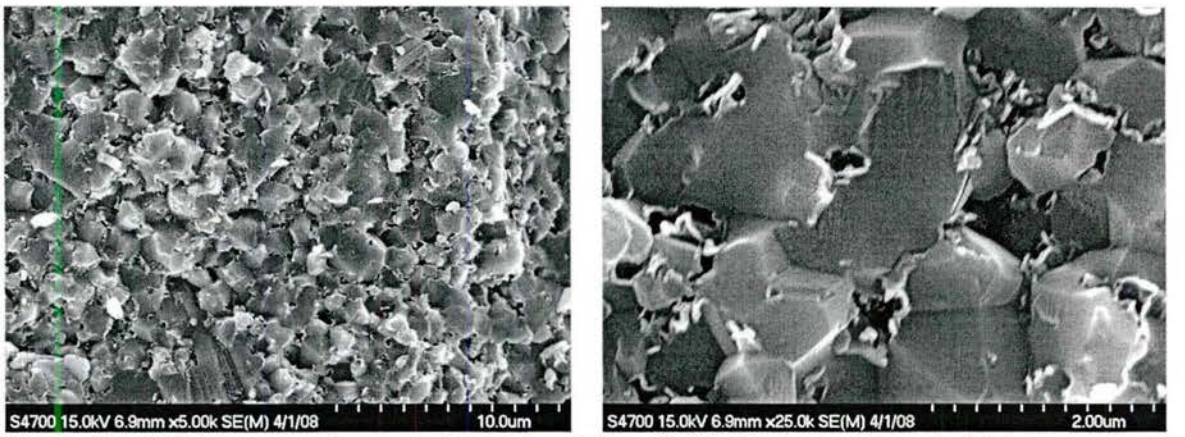

Figure 2. SEM images of composites sintered from P-55. Carbon-rich material is present on the grain boundaries of the ceramic.

Powder P-56, which had Fe nanoparticles present and was carbonized, was also sintered to near full density (Figure 3). Measurements indicated that the density was ~97% after sintering at 1600°C. Unlike the P-55 material, a few isolated regions that had high concentrations of CNTs were observed as shown in the lower right side of the image on the left. Higher magnification imaging showed that the grain boundary structure of the P-56 material was similar to that of the P-55 material, indicating that the carbon observed in these areas may, in fact, be excess carbon and not CNTs that were grown in-situ. Based on the similarities with the P-55 material, the CNTs may be isolated to the agglomerated regions, with the carbon between the grains being mainly amorphous carbon that formed during the carbonization step. Based on TGA analysis showing a 1.5% weight loss, the P-56 material should contain ~2.9 vol.% carbon. The maximum content of CNTs would be ~2.9 vol.%. However, if the P-56 material contains roughly the same amount of amorphous carbon as the P-55 material, then the CNT content could be as low as ~1.5 vol.% with the balance of the carbon (total C content ~3 vol.%) present in other forms.

To complement the materials supplied by Hy-Tech, a composite powder was prepared at Missouri S&T using the same alumina powder used at Hy-Tech and 3 vol.% CNTS from a commercial vendor. The CNTs were purified using the procedure reported in the January 2008 report and then dispersed with the alumina powder. The powders were freeze-dried to minimize segregation, pressed, and then sintered using the same conditions as the other materials. Based on bulk density measurements the Missouri S&T materials indicated that they sintered to ~98% relative density. Some areas of CNT segregation were observed, but the CNTs were generally distributed uniformly around the individual Al_2O_3 grains.

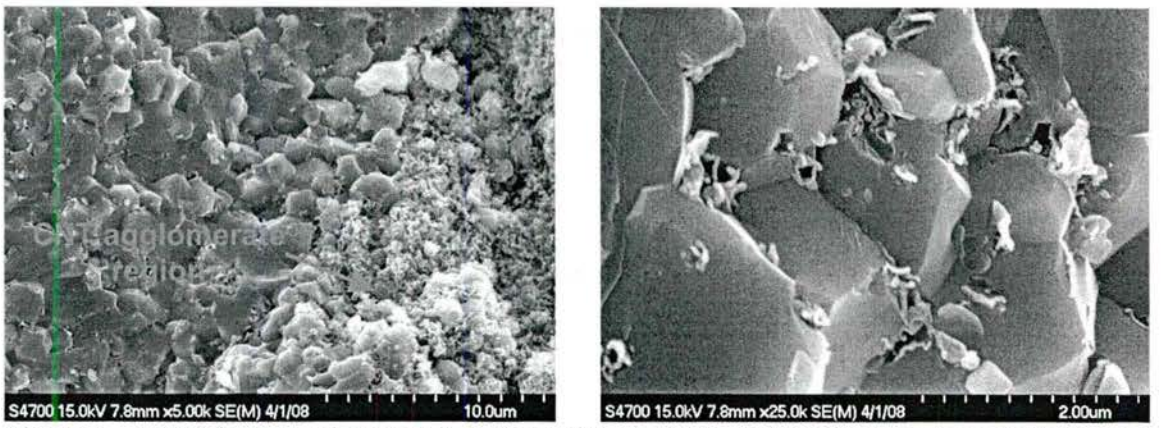

Figure 3. SEM images of composites sintered from P-56. A few, large regions that appear to be CNT agglomerates were observed as well as carbon rich material present on the grain boundaries.

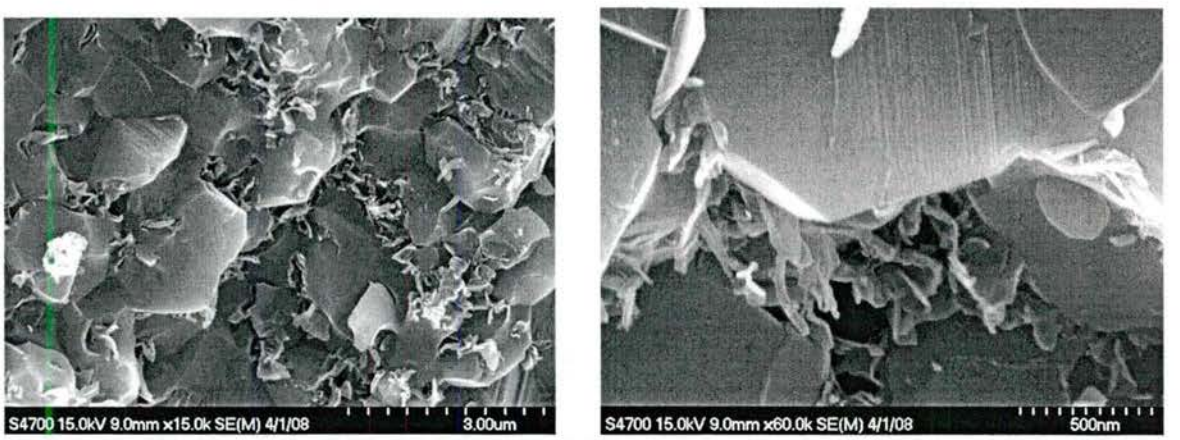

Figure 4. SEM images of Al_2O_3-CNT materials containing 3 vol.% CNTs prepared at Missouri S&T. The CNTs showed some agglomeration along grain boundaries, but were well-dispersed in most areas.

In addition to density, the microhardness, elastic modulus, flexural strength, and fracture toughness were measured for the sintered Al_2O_3-CNT composites. The properties are summarized in Table 1. Testing of the Missouri S&T material is not yet complete, but the other materials are compared. Because of the lower total carbon content, the materials prepared from P-55 have higher hardness, modulus, and strength. The large drop in strength for P-56 is likely due to both the amount of carbon present as well as the relatively large size of some of the carbon inclusions. It is likely that a material with the same carbon content, but with a uniform distribution of the carbon would have a strength much closer to the value of the P-55 material than the P-56 material. However, the higher carbon content of the P-56 material does give it higher fracture toughness.

Beyond the measured properties, incorporation of carbon has a significant effect on the fracture behavior of the alumina. Figure 5 compared optical micrographs of the surfaces of the

composites after hardness indentation. As shown in the figure, the distribution of carbon in P-55 is uniform. Cracks that emanate from the corners of the hardness indentation appear to be arrested by intersecting with the carbon inclusions. The carbon distribution is not as uniform in the P-56 material. As a result, cracks display different behavior depending on the local carbon content. For example, indents in areas of uniform, fine carbon inclusions are blunted close to the source. In contrast, indentations in areas with lower carbon content result in longer cracks. Because crack length is a qualitative indication of toughness (inverse relationship), the toughness appears to be higher in areas with uniform carbon distribution. The measured values of toughness (determined by measuring the retained strength of specimens after indentation) provide quantitative corroboration of the qualitative assessment based on crack length. The material prepared at Missouri S&T has a uniform distribution of carbon, which may provide a better balance of strength and fracture toughness. Efforts are underway to prepare test bars to complete this part of the testing matrix.

Table 1. Summary of physical and mechanical properties of Al_2O_3-CNT composites.

Material	Relative Den. (%)	Carbon (vol.%)	Hardness (GPa)	Modulus (GPa)	Strength (MPa)	Toughness ($MPa \cdot m^{1/2}$)
Hy-Tech P55	98	1.5	19	300	439 ± 32	3.5 ± 0.1
Hy-Tech P56	97	2.9	18	313	244 ± 18	4.1 ± 0.2
MS&T #1	98	3.0	17			

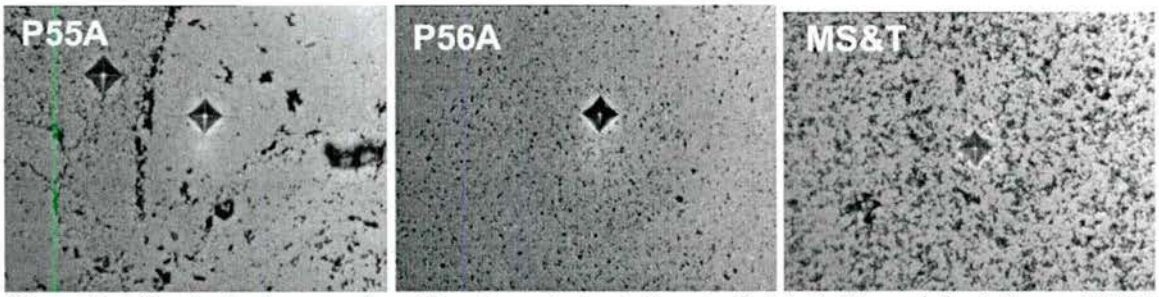

Figure 5. Optical micrographs of hardness indentations in P-55, P-56, and the Missouri S&T materials.

SiC Pellets for Sintering

A series of SiC pellets were prepared for sintering experiments. The composition and sintering additives were selected based on the research of Yoshimura et al. (H.N. Yoshimura, A.C. Da Cruz, Y. Zhou, and H. Tanaka, "Sintering of 6H(α)-SiC and 3C(β)-SiC Powders with B_4C and C Additives," Journal of Materials Science, 27 1541-1546, 2002) who reported that fine grained SiC could be produced by pressureless sintering at 2100°C using a combination of B_4C and C as sintering additives. Pellets were batched with 0.4 wt.% B_4C and enough phenolic resin to produce 1.8 wt.% carbon. The powders were charred at 800°C in vacuum. Pellets were prepared by uniaxial pressing (~30 MPa) followed by cold isostatic pressing (~200 MPa). The pellets were charred at 800°C in vacuum prior to shipment to Hy-Tech. In continuing studies at Missouri S&T, pellets will be densified by conventional sintering in a graphite element furnace.

LaB_6-ZrB_2 Eutectic Pellets

A LaB_6-ZrB_2 eutectic powder mixture was prepared with the ratio 79 wt.% LaB_6 to 21 wt.% ZrB_2. A small amount (~0.5 wt.%) B_4C was added to batch to remove oxygen during heat treatment. The LaB_6 powder was supplied by H.C. Starck with a starting particle size of -325 mesh while the ZrB_2 was H.C. Starck grade B powder with a starting particle size of ~2 μm. The LaB_6, ZrB_2, and B_4C were ball milled in hexane with for 48 hours to blend the materials and reduce the size of the LaB_6. The powders were uniaxially pressed at ~30 MPa into 0.75 inch diameter pellets. The pellets were further compacted by isostatic pressing at ~200 MPa prior tor shipment to Hy-Tech. An additional specimen that was a 1.0 inch diameter, 1.0 inch tall right regular cylinder was pressed and shipped to the Y12 plant in Oak Ridge, TN for dielectric measurements.